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(54) MEMBRANES ELECTROLYTES COMPOSITES POUR PILES A COMBUSTIBLE

(54) COMPOSITE ELECTROLYTE MEMBRANES FOR FUEL CELLS

(57)
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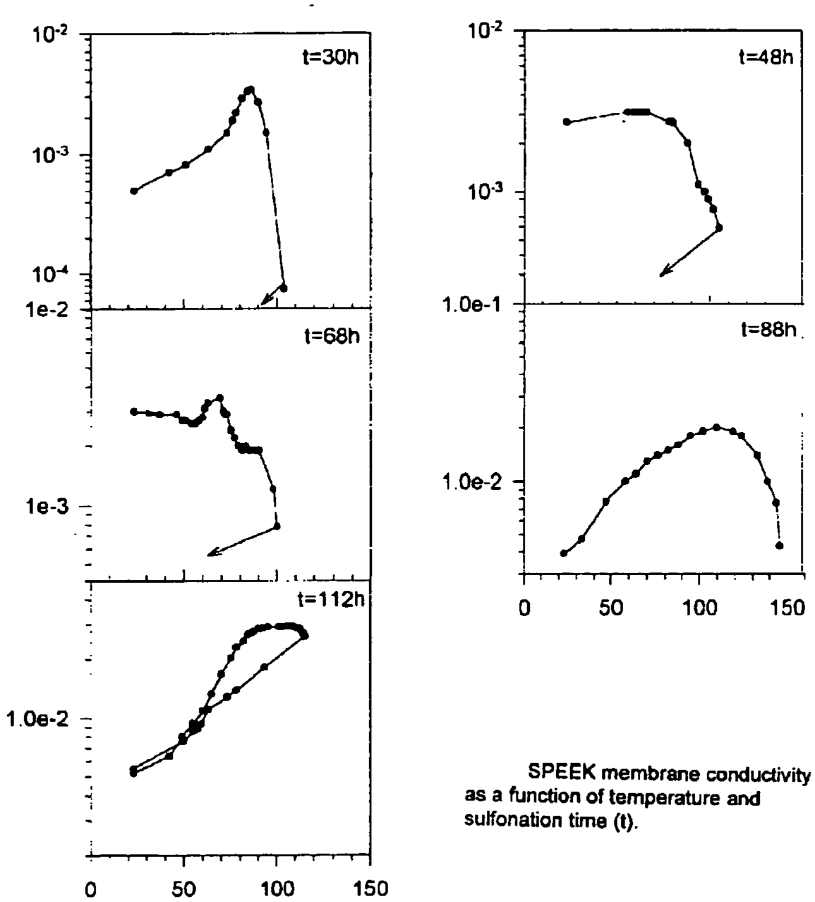

SPEEK membrane conductivity as a function of temperature and sulfonation time (t).

(57) It is proposed to prepare fuel cell membranes consisting of a solid electrolyte embedded in a polymer matrix. These membranes will provide a barrier to the diffusion of methanol from the anode to the cathode and they will provide a high proton conductivity.

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ABSTRACT

It is proposed to prepare fuel cell membranes consisting of a solid electrolyte embedded in a polymer matrix. These membranes will provide a barrier to the diffusion of methanol from the anode to the cathode and they will provide a high proton conductivity.

TITLE: COMPOSITE ELECTROLYTE MEMBRANES FOR FUEL CELLS

Field of Application: Fuel cells as non-polluting, high thermal efficiency, alternative energy sources for stationary and mobile applications

Commercial Applications: Using this invention will significantly reduce the production cost of the methanol fuel cell while improving its performances thus speeding up its commercialization

Summary of the invention:

It is proposed to prepare fuel cell membranes consisting of a solid electrolyte embedded in a polymer matrix. These membranes will provide a barrier to the diffusion of methanol from the anode to the cathode and they will provide a high proton conductivity.

Description of the invention:

A fuel cell is an almost ideal energy source yielding a very high thermal efficiency and an essentially zero release of atmospheric pollutants. In transport applications, the direct methanol fuel cell (DMFC) is presently considered as most appropriate and promising.

Up to now only perfluorinated ionomers (PFI) membranes were considered to meet the requirements of polymer electrolyte membrane (PEM) fuel cells, namely a high proton conductivity, a high stability in the cell operating conditions and a high durability. The PFI currently utilized in PEM membranes have however some drawbacks which prevent their commercial application on a large scale. First of all these ionomers are very expensive. For example, the manufacturer's price for the NAFION membranes (Dupont de Nemours) which are the most utilized ones at the laboratory scale exceeds 600 US$/m^2. Other membranes of this kind (DOW, RAI, ...) are still more expensive (up to 2000 US$/m^2). In addition a serious drawback of these materials is their high permeability to methanol which allows an easy transport of this fuel from the anode to the cathode. This phenomenon reduces significantly the cell performance and must be eliminated before DMFC can be commercialized.

Currently, the search for alternate polymeric products which would be less expensive than PFI has become a major concern of researchers in the fuel cell field.

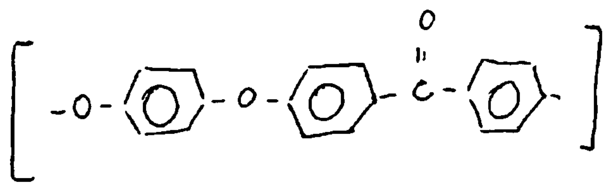
The properties that are required for DMFC membranes are as follows:

- A high proton conductivity of at least 5×10^{-2} S/cm in order to avoid Ohmic losses.
- A good mechanical resistance of films of 100 μm thickness.
- A low permeation of reactants and products of the electrochemical combustion.
- A high chemical and electrochemical stability in the cell operating conditions.
- A cost compatible with commercial requirements.

The approach we used in our research is based on the general principle of composite materials, which is to combined the properties of each of the two components to reached a desired set of properties for the composite material. Most of the known proton conductors are not appropriate for the fabrication of membranes, being too fragile and of little mechanical resistance as a film. Electrolyte membranes can however be prepared with a polymer matrix. It is professor E. SKOU of the University of Odense (Danmark) who proposed to use a composite membrane in fuel cells. The studies of his group were however essentially oriented toward the use of zeolites as proton conductors. The best ones they identified were tin modified mordenites. These studies were stopped in the mid nineties' without reaching their objectives. In particular this group never reached a high enough proton conductivity.

Our group began its activities on fuel cell membranes in 1995 by a systematic study of the electrical properties of zeolites. Then we broadened our field of investigations by including some salts of oxo-acids in the list of solid electrolytes of interest. The compound we will propose for patenting is boron phosphate which gives a high membrane conductivity. In presence of water wafers of BPO_4 have a conductivity higher than 10^{-2} S/cm and depending on the conditions of its preparation it can reach a high stability in aqueous media. The electrical properties of BPO_4 are strongly dependent upon preparation and pretreatment conditions. In proton conducting membranes it is proposed to use powdered BPO_4 synthesised at 120°C, with a particle size of 60 mesh and calcined at 400-500°C.

As an example of the polymer matrix to be used in the composite membrane, we suggest a poly-aryl ether ether ketone (PEEK), a rigid and thermally stable thermoplastic. Its formula is as follows:



PEEK hydrophobic character does not allow its use as solid electrolyte in the presence of water. In order to make PEEK more water compatible and to give it proton conduction properties we sulfonated PEEK in concentrated sulfuric acid. It must be noted that the chemical stability of sulfonated PEEK (SPEEK) decreases, as for essentially every polymer, when the level of sulfonation is raised. Highly sulfonated SPEEK becomes for example partly soluble in methanol. The level of sulfonation of SPEEK should not exceed 70% so that it stays chemically stable. Even partially sulfonated SPEEK reaches a rather high proton conductivity. Figure 1 shows the variation in SPEEK conductivity with temperature. It is seen that even in absence of solid electrolyte, SPEEK samples have a rather high conductivity which depends strongly on the duration of the sulfonation process. In particular the sample treated for 112 h shows a conductivity of the order of 3×10^{-2} S/cm which remains reversible even once the sample has been heated to 120°C. For the other samples (sulfonated for a shorter time) this conductivity is not stable and it drops irreversibly after heating to 100-120°C.

The composite membranes were fabricated as follows:

Powdered BPO_4 was dispersed in a dimethyl acetamide (DMA) solution of sulfonated PEEK and stirred for 24-48 hours. After evaporation of the solvent, the polymer/BPO_4 blend is spread over a glass plate and dried for 12 hours at room temperature, then for 8 hours at 40°C and another 12 hours at 120°C under vacuum, to eliminate any trace of DMA. Before their conductivity was measured, the membranes were stabilized by immersion for several hours in water, which increases their proton conductivity. As shown in Figure 2 the conductivity of the composite membranes is higher than the one of pure SPEEK membranes (compare with Figure 1). It is important to note that the conductivity of the composite membranes is more stable thermally than the one of SPEEK membranes. Heating to 100-120°C does not lead to a conductivity drop.

We believe that composite BPO_4/PEEK membranes are very promising for the fabrication of fuel cells. These membranes may indeed be utilized as electrolyte separating the anode from the cathode and they may be used over the temperature range of 100-120°C. Usually PEM fuel cells work at temperatures not exceeding 80°C. These membranes being stable at higher temperature should be very stable in the working conditions of the cell.

Unfortunately it was not yet possible to test these membranes in a real fuel cell.

As a concluding remark, the new claims of this work are:

- Use of BPO_4 as a solid electrolyte in a polymer matrix.
- Specific conditions for the preparation and pretreatment of appropriate BPO_4.
- Use of PEEK as a matrix of the composite membrane.
- Conditions of PEEK sulfonation.
- Conditions for the preparation of polymer/BPO_4 composite membranes.

Previous articles:

Even though numerous publications deal with fuel cell membranes, only a very small number of them are dedicated to composite membranes. One must first mention the work of Prof. SKOU discussed above:

- N. Knudsen, E.K. Andersen, I.G.K. Andersen, E. Skou, Solid State Ionics, 28-30 (1988) 627.
- N. Knudsen, E.K. Andersen, I.G.K. Andersen, E. Skou, ibid., 35 (1989) 51.
- J. Kjaer, S. Yde-Andersen, N.A. Knudsen, E. Skou, ibid., 46 (1991) 169.
- N. Knudsen, E.K. Andersen, I.G.K. Andersen, P. Norby, E. Skou, ibid., 61 (1993) 153.
- N. Rao, T.P. Andersen, P. Ge, ibic., 72 (1994) 334.

Moreover one Korean group describes some heteropolyacid/polyethersulfone membranes:

- M.W. Park, J.C. Yang, H.S. Han, Y.G. Shul, T.H. Lee, Y.I. Cho, Denki Kagaku, 64 (1996) 743.

These membranes are most probably impossible to use commercially due to their lack of stability in the cell conditions. There is also one US patent application:

- Membrane, containing inorganic fillers and membrane and electrode assemblies and electrochemical cells employing same. W.G. Grot, WO96/29752, 26 September 1996.

We believe this application is likely not be accepted as it makes use of Nafion (PFI, already the common practice) and a solid which does not contribute to any enhancement of protonic conductivity compared to Nafion. Contrary to our case, this solid is only a filler and its role is only to decrease the mass of polymer utilized in the membrane.

Our invention has never been entirely disclosed. We have published the results of tests performed on membranes made of various other polymers such as polyethersulfone, polymethylmethacrylate and polyether imide :

- J. Zaidi, S.D. Mikhailenko, S. Kaliaguine, Symp. Proc., Colorado Springs, July 1998.

These membranes have lower conductivities compared to SPEEK membranes, and poor mechanical properties.

The high conductivity of BPO_4 wafers was disclosed in a scientific paper, with no mention of its possible use in composite membranes:

- S.D. Mikhailenko, J. Zaidi, S. Kaliaguine, J. Chem. Soc. Faraday Trans., 94(11) 1613-1618 (1998).

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List of appendixes

1. J. Kjaer, S. Yde-Andersen, N.A. Knudsen, E. Skou, Solid State Ionics, 46 (1999) 169.

2. N. Rao, T.P. Andersen, P. Ge, Solid State Ionics, 72 (1994) 334.

3. M.W. Park, J.C. Yang, H.S. Han, Y.G. Shul, T.H. Lee, Y.I. Cho, Denki Kagaku, 64 (2996) 743.

4. W.G. Grot, G. Rajendran, Membranes containing inorganic fillers and membrane and electrode assemblies and electrochemical cells employing same, US Patent application PCT/US96/03804, 26 September 1996.

CLAIMS:

1. A fuel cell comprising a composite membrane having a polymer matrix, wherein BPO_4 is used as a solid electrolyte in said polymer matrix.

2. The fuel cell of claim 1 wherein said composite is a BPO_4/ PEEK membrane.

3. The fuel cell of claim 1 or 2, wherein said fuel cell can operate at temperatures above 80°C.

4. The fuel cell of claim 3, wherein said membrane can withstand temperatures of about 100-120°C.

5. A polymer matrix comprising poly-aryl ether ether ketone (PEEK).

6. Use of a BPO_4 as a solid electrolyte for the manufacture of a polymer matrix.

7. Method of making a thermally stable composite membrane comprising:
   a) a dispersion of a BPO_4 in a solution including sulfonated PEEK and a solvent;
   b) evaporation of said solvent to yield a BPO_4 polymer and;
   c) a spreading and drying of said BPO_4 polymer,

thereby yielding a thermally stable composite membrane.

8. Use of PEEK as a matrix to manufacture a thermally stable composite membrane.

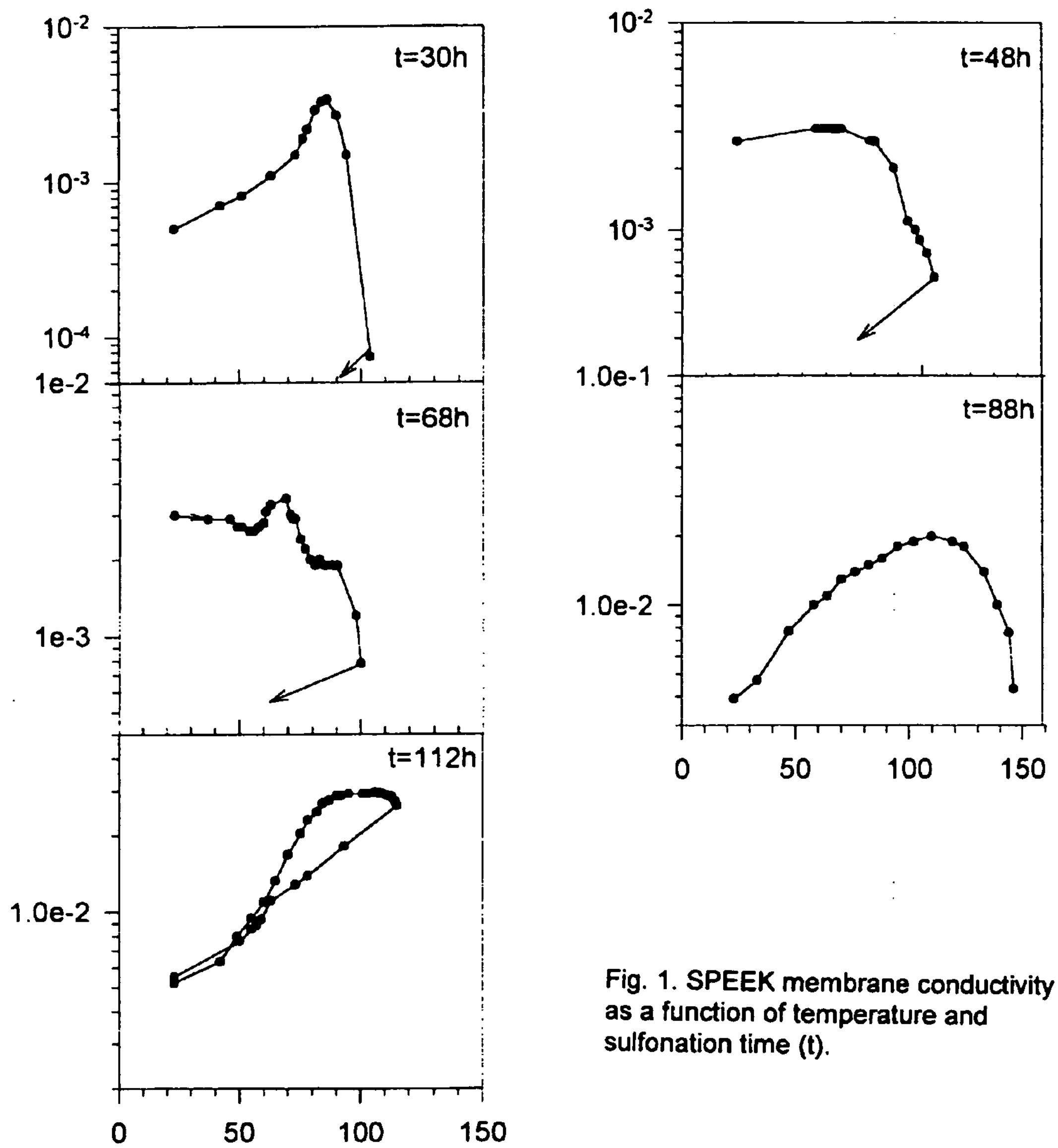

Fig. 1. SPEEK membrane conductivity as a function of temperature and sulfonation time (t).

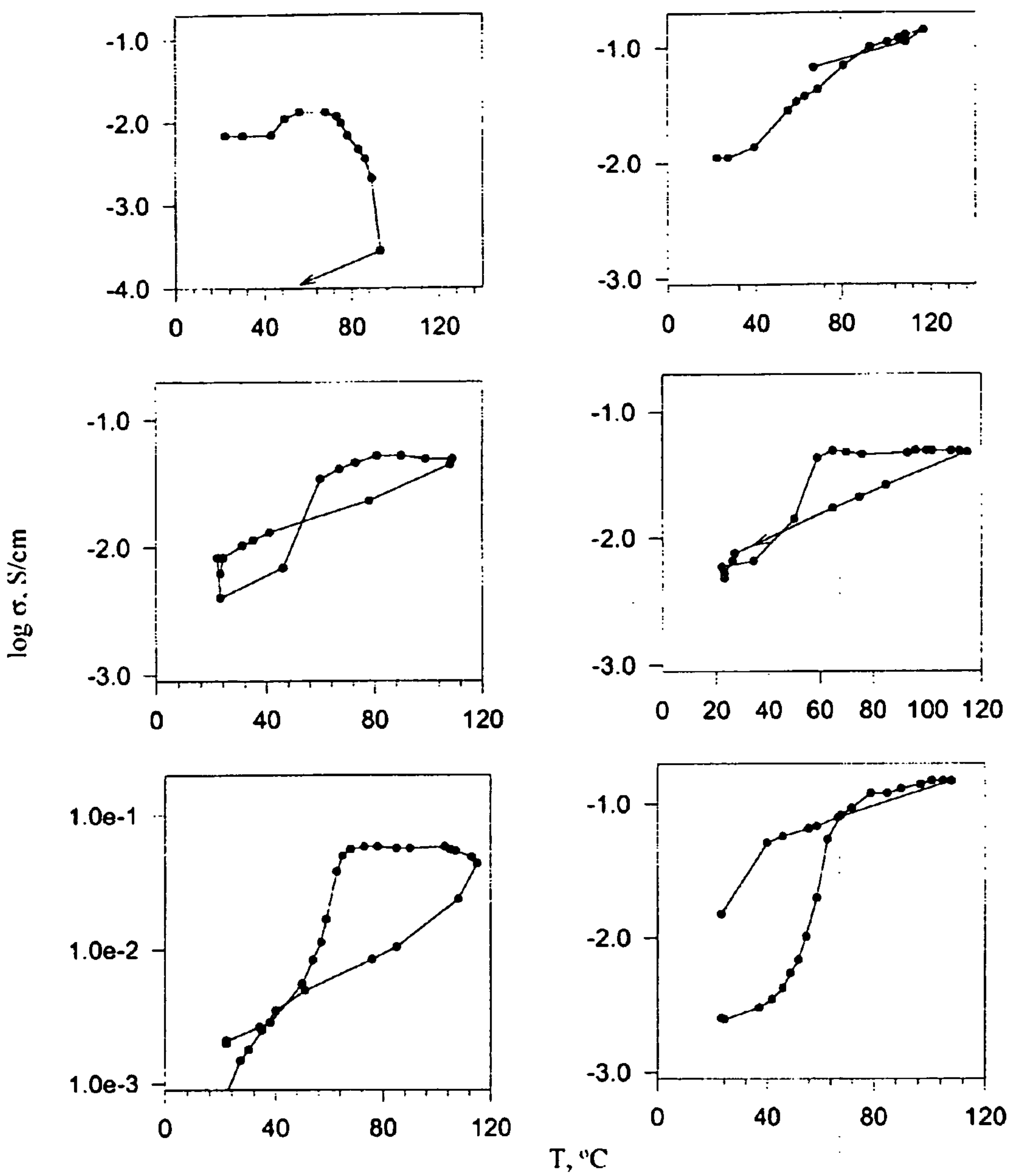

Fig. 2 . Conductivity of the composite membranes as a function of temperature and BPO_4 content.